

## Process for the preparation of paints to be exposed to bad weather

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Abstract available for DE19910876

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A process for the production of weather-resistant coatings on glass, metal or polymer surfaces etc. comprises the hydrolytic condensation of hydrolyzable silicon compound (s), in which 20-100 mol % of the starting material consists of a hydrolyzable organosilicon compound with a blocked isocyanate residue. A process for the production of weather-resistant coatings on substrates such as glass, metal or polymer surfaces involves the hydrolytic condensation of hydrolyzable silicon compound (s), 20-100 mol % of which consist of a compound of formula  $X_m-Si-R_4-m-Y_n$  (I), in which X = H, halogen, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl or NO<sub>2</sub>; n = 1 or 2; RE = H and / or alkyl; R = alkyl, alkenyl, alkynyl, aryl, arylalkyl, alkylaryl, arylalkenyl, alkenylaryl, arylalkynyl or alkynylaryl (all optionally containing in chain-O-, -S-, NO<sub>2</sub>- or -NHCOO- groups and / or optionally substituted with halogen, optionally substituted amino, amide, aldehyde, keto, alkylcarbonyl, carboxy, mercapto, cyano, hydroxy, alkoxy, alkoxycarbonyl, sulfonic acid, phosphoric acid, (meth) acryloxy, epoxide or vinyl groups); Y = a blocked isocyanate group; m, n = 1-3.

### Description of DE19910876

The invention concerns a procedure to the production of a bewitterungsbeständigen coating with one coating from a hydrolysierbaren silicon connection is raised which shows a kovalent engaged, blocked Isocyanat.

Coatings on substrates on the base of hydrolysierbaren silicon connections are known. In particular the material class of the so-called "ORMOCERE" became detailed during the last years, in particular with reference to coatings of different substrates examined. In the EP 0 450 625 A1 a such "ORMOCERE" coating is described for coating by plastic substrates. On this occasion, hydrolysierbare silicon connections on a substrate are produced, hardened by radiotherapy and afterwards submitted to a thermal Nachhärtung. Other such procedures and coatings are known from the EP 0 365 027 A2 as well as from the DE 38 36 815.

Disadvantageously with all these, up to now from a standing position of the technology to known hybrid Sol gel layers (ORMOCERE) it is that the layers accessible up to now could not be used in the undeveloped outskirts area, because under the influence of light, humidity and/or temperature change no stable layers were available.

Outgoing from this it is to be given the task of the present invention a new procedure for

producing by coatings on substrates, indeed, should be based on the base up to now in the state of the technology to known hybrid Sol gel layers with (ORMOCERE) which leads, however, to layers which are also under Bewitterungsverhältnissen like they in the undeveloped outskirt area, for longer time remain stable.

The task is solved by the characteristic signs dea of patent claim 1. The unterclaims indicate advantageous continuing education.

Erfindungsgemäss the application is suggested therefore by blocked Isocyanatosilanen in the Sol gel process. Only by temperature rise becomes the Isocyanat deblockiert and can enter with different partly known other hydrolysierbaren silicon connections and/or metal connections and/or organic polymers linking reactions. Besides, the most important ones are the conversion with Hydroxygruppen, amine, water and those of the respective reaction products with an other Isocyanat. In Fig. 1 a suitable reaction pattern which shows the reaction possibilities of the Isocyanate with amine, water and Hydroxygruppen is returned.

Now astonishing proofs it has turned out that the coatings which have been produced with such blocked Isocyanatosilanen show überlegene qualities concerning the liability, Vergilbung, tear education and the brilliant loss. The Anmelderin could show that the new layer materials are stable up to 1500 hours in the QUV B test (40 C DEG / 60 DEG C) without recognizable change.

Erfindungsgemäss is so produced the bewitterungsbeständige coating that the hydrolytische condensation with from 20 to 100 Mol-% preferentially from 50 to 90 Mol-%, covered to the monomeren source components a hydrolysierbare silicon connection of the general formula I is carried out, and

$X_m-Si-R_4-m-Y_n$  I

it is used. Besides, the rests in the general formula I have the following meaning:

X it is same or has passed away and can signify hydrogen, halogen, Alkoxy, Acyloxy, Alkylcarbonyl, Alkoxycarbonyl or NO. ' 2 (RE-H and/or Alkyl) and the rests R which immediately or can have passed away Alkyl, Alkenyl, Alkynyl, Aryl, Arylalkyl, Alkylaryl, Arylalkenyl, Alkenylaryl, Arylalkynyl or Alkynylaryl explain and these rests can be interrupted by O-or S-atoms or the GROUP NO. ' or NHC (O) O-and one or several Substituenten from the group of the halogens and if necessary substituierten Amino-, Amid-, aldehyde, Keto-, Alkylcarbonyl-, Carboxy-, Mercapto-, Cyano-, Hydroxy-, Alkoxy-, Alkoxycarbonyl, Sulfonsäure-, phosphorus acid, Acryloxy-, Methacryloxy-, Epoxy or vinyl groups can carry and Y blocked Isocyanat is with m = from 1 to 3 and n = from 1 to 3. With the connections of the general formula I are especially preferred: with 3,5-Dimethylpyrazol or with 1,2,4 Triazol blocked 3-Isocyanatopropyltriethoxysilan.

How it arises from the general formula I, the rest R in the silicon shows from 1 to 3 Isocyanatgruppen. These Isocyanatgruppen can be moved with all blocking reagents from a standing position known the technology up to now for Isocyanate and be blocked thus. Two examples are in Fig. 2 returned. Besides, the Isocyanatosilan was moved in stöchiometrischer amount with 3,5 Dimethylpyrazol and 1,2,4 Triazol. Then the so preserved blocked Isocyanatosilane can be used without other cleansing steps for synthesising of the coating systems.

As protrudingly described to made blocked connections then can be Co.-condensed with every kind of hydrolysierbaren silicon connections and metal alc. oxide to generate an inorganic network. Also an interlinking with purely organic connections is possible.

Preferential connections with those the blocked Isocyanatosilane can be moved, are defined by the general formula II

$X_m-Si-R_4-m-Z_n$  II

Besides, in the formula II the rests X, R own and the index m the same meaning as protrudingly with the general formula I given during n from 1 to 4 can be. The rest Z can carry on it one or

several Hydroxygruppen, an amino group or an Epoxyfunktion. Then these connections are able to like in the reaction pattern to Fig. 1, with the blocked Isocyanat are moved. Is preferred, on this occasion, if connections of the general formula II are used which dispose of several functional groups Z, i.e., e.g., so-called Silanpolyole or Silane which carry several NH<sub>2</sub> groups or Epoxygruppen. In the Fig. From 3 to 6 preferential production examples from such hydroxyfunktionalisierten Silanen and Epoxyverbindungen are given. Fig. Besides, the addition reaction of Mercaptosilan shows 2 in Epoxypropanol, Fig. 4 the addition reaction of 3-Aminopropyltriethoxysilan (AMEO) in Epoxypropanol and Fig. 5 the synthesis hydroxyfunktionalisierten Polysiloxans. Fig. The reaction pattern of the synthesis of a Silans from the Edukten Isocyanatopropyltriethoxysilan and Epoxypropanol returns 6.

In the production of the bewitterungsbeständigen coating after the invention it is also possible, known as before already from the hybrid Sol gel chemistry in the state of the technology, that the Hydrolyse in present of from 0 to 40 Mol-% of a metal connection of the general formula III

MeRx III  
it is carried out. Examples of metals are, on this occasion, a tin, titanium, zircon and aluminium. The rest R immediately or can have passed away, is selected from halogen, Alkoxy, Alkoxy-carbonyl and Hydroxy and it is also possible that some of these rests can be substituted all or part with a Chelatliganden. For the case that the metal is aluminium is X immediately 3 and for the cases for which the metal titanium, tin and zircon is, is X immediately 4.

To emphasise especially with the erfindungsgemässen production procedure it is that also, in addition, still before, during or after the Hydrolyse an organic connection (cannot be added silicon-containing). In this case it is only necessary that the organic connection shows at least one Hydroxygruppe, an amino group or an Anhydridfunktion, so that a suitable reaction with deblockierten Isocyanat can be carried out. Special examples for this are Benzol-tricarbonsäureanhydrid (BTCA), Tris-(Hydroxyethyl)-Isocyanurat, 2.2-to (4 Hydroxycyclohexyl) a propane (hydrogenated Bisphenol A, HBPA).

In the production of the bewitterungsbeständigen coating the hydrolytische condensation can be carried out with the protrudingly closer described Edukten in an actually known way also in present of a sour or basischen condensation catalyst. Basically can be also added with the procedure after the invention with the Hydrolyse additives which are selected from organic connections, course means, colouring, UV stabilizers, fillers, viscosity regulators, lubricants, net means, Antiabsetzmittel and/or oxidation inhibitors or mixtures of it. Concerning the condensation catalysts and the additives the DE 38 36 815 as well as to the EP 0 450 625 A1 is referred to the revelation salary.

Furthermore it is advantageous if with the erfindungsgemässen coating procedure the substrate surface is pretreated before the application of the coating material. As a pretreatment procedure all pretreatment procedures known from a standing position up to now the technology are possible, on this occasion, especially the application of a Primers, i.e. of a custody mediator or procedure with those the surface ausgeheizt, is leached out or is precleaned by means of watery or organic media and/or put out to an electric unloading.

Besides, to the age-hardening of the coating it is planned to put out this one warm treatment at a temperature of from 120 to 300 C DEG. As in the state of the technology up to now with already known hybrid Sol-gel layers described, a treatment with radiation can also occur as a function of the source systems mainly with IR, UV or with microwaves.

The invention is described in the following on the basis of execution examples closer.

#### Example 1

Example 1 concerns the production of the system I from DMP-IPTES, GPTES and BTCA (Benzoltricarbonsäure-anhydrid) which became mixed and with the stöchiometrischen quantity of water hydrolysiert. The Edukte were comparatively used by a part BTCA to three parts DMP-IPTES and three parts GPTES. The Hydrolyse was catalyzed by the used carboxylic acid BTCA. The possible interlinking reactions are returned in fig. 7.

The coating material was hardened 45 min with 180 C DEG. The layers were steady and clear, the layer thickness amounted to 3  $\mu$  m. The mechanical qualities were determined with the help of mike hardness measurements. To improve further the mechanical qualities, it was added with the synthesis Tetraethoxysilan (TEOS) for the rise of the inorganic across interlinking in two different amounts. These became 2 (system Ia) or 4 parts (system Ib) TEOS, covered to the used material amount of the aromatic acid, added. The universal hardness and the other mechanical characteristics could be improved by this change clearly (tab. 1).

Tab. 1

Change of the universal hardness with increasing TEOS salary (45 min with 180 C DEG getempert)  
EMI9.1

The stability of the systems compared with humidity is high. A short-term test of 4-day condensation climate check has shown that no changes of the layers appear.

Hence, system I and his variations offer a new excellent possibility to produce hybrid coating materials which also show stability compared with humidity beside excellent mechanical permanence. They distinguish themselves by the exclusive application of Ethoxysilanen also by methanol freedom.

## Example 2

Example 2 shows the synthesis of the system II. As an Edukte BTCA and the blocked Isocyanatosilan (DMP-IPTES) comparatively became 1: 3 uses. DMP-IPTES was used in the profit to move the Carboxylgruppen very completely. Überschüssigen Isacyanatgruppen different other interlinking reactions can come (cf. Fig. 1).

The synthesis runs as from system I. The Hydrolyse is concluded after 1 h response time with RT. A comparison of the Ir spectra of the Beschichtungssols and the hardened layer showed that the gang typical for 5-ring-Imide originates with 1,770  $\text{cm}^{-1}$  while hardening. Even more clearly than the Ir spectra showed the Raman spectra the forming of the Imidverknüpfungen with the Härtingsprozess.

From the spektroskopischen investigations can be closed that the organic interlinking has taken place in the desired sense. Fig. 8 shows the likely reaction expiry. The reaction runs off in three steps. First become the Isocyanatgruppen deblockiert. As a result these react with the Carboxylgruppen under splitting off of  $\text{CO}_2$  to Amiden. As a result a part of the Amidgruppen can form under splitting off of water with a Carboxylfunktion located in ortho position cyclisches Imid.

The layers are hard after the thermal Härting of 30 min with 180 C DEG and are clear. The mechanical qualities were examined with the help of the mike hardness measurement. Tab. 2 summarises the results.

Tab. 2

Mechanical characteristics of system II (30 min with 180 C DEG hardened)  
EMI11.1

Example 3

The system III corresponds basically system II. Nevertheless, instead of a third in system II used amounts DMP-IPTES it was used APTES. This has the advantage that an Amid from BTCA and APTES can be formed before the Härtungsschritt (Fig. 9).

This conversion was carried out before the Hydrolyse to prevent an opening of the Anhydrides by water. The whole reaction mixture was used, in the end, hydrolysiert and for coating. The reaction course is in Fig. 8 similarly, it only less blocking means (DMP) and CO<sub>2</sub> are released by which the shrivelling inclination decreases during the Härtungsreaktion. Thus layer-thick can be reached above 10 µm.

The layers are clear and hard. The mechanical qualities were examined again with the help of the mike hardness measuring instrument. Tab. 3 summarises the results. They correspond possibly to those of system II.

Tab. 3

Mechanical characteristics of systems III (30 min with 180 C DEG hardened)  
EMI12.1

System III is free of methanol like system II and can be stored with RT, without undesirable reactions take place. The reactive organic groups are protected (blocked Isocyanate) or have already reacted (Amid education).

Example 4

The systems described up to now with DMP-IPTES use for hardening either a combination of many reactions from which one is the old ethane education, or the Isocyanat as the verkapptes amine with whose help Imide or Amide originate. In the difference in addition the system IV is a coating system which owns excluding old ethane linkings as organic connections. Were used in addition only Edukte which contain aliphatische or cycloaliphatische groups. Thereby is the construction of the system him 1K--or polyurethane varnish 2K similarly which is used and a. in the car industry as bewitterungsstabile systems.

System IV exists of a Co-Hydrolysat from DMP-IPTES and ASB to which was added for the organic interlinking Tris-(hydroxyethyl)-isocyanurat (THEIC). Fig. The Triol component THEIC and the product of the Härtungsreaktion of the system shows 10.

The mechanical qualities of layers were determined like in the preceding investigations with the help of mike hardness measurements (table 4).

Tab. 4

Mechanical characteristics of system IV (30 min with 180 C DEG hardened)  
EMI13.1

With the storage with RT the hardness of this system changes. Table 6 shows the change after 3.5 months of storage with RT.

Tab. 6

Mechanical characteristics of systems IV (30 min with 180 C DEG hardened) after 3.5 months of storage with RT  
EMI13.2

Example 5

System V is a variation of formulation IV. Instead of the triply linking up THEIC propane was used as a hydroxygruppen weight-bearing component 2.2-to (4-hydroxycyclohexyl). The connection can be also called hydrogenated Bisphenol A (HBPA).

On account of in comparison to system to IV expected more wide-meshed, organic linkings the inorganic interest was raised to the balance. Beside 50 mol-% DMP-IPTES were used 30 mol-% ASB and 20 mol-% TEOS. The relation of blocked Isocyanatzu Hydroxygruppen amounted 1.2: 1. The mechanical qualities of a layer which were received after Härtung with 180 C DEG are shown in table 6.

Tab. 6

Mechanical characteristics of system V (45 min with 180 DEG C)  
EMI14.1

On account of the high inorganic interest system V is harder than a system IV.

Bewitterungsbeständigkeit of system IV and V

To the investigation of the Bewitterungsbeständigkeit the QUV B test of the company Q-Panel was carried out. As a substrate aluminium was used. The tests are irradiated cyclisch 4 h with 40 C DEG with water betaut and 4 h with 60 C DEG drily with UV B light. They are put out beside the load by humidity and ultraviolet light also to a regular temperature and humidity change.

The systems IV and V became 1500 h in the QUV B test bewittert. In different time intervals tests were taken from the test and were characterised.

Already by the visual judgement of the tests is to be recognised that the layers own a high degree of Bewitterungsstabilität. Also after 1500 h no serious damages of the surface (are to be recognised how Vergilbung, tear education, separation).

Change of the shine during the Bewitterung

Because coatings not only protective requirements have to be enough, but to fulfil decorative tasks in most cases also, the optical impression may also not change after Bewitterung seriously. Brilliant measurements are good means to grasp the optical impression measuring-technically

and to quantify changes. Because the degradation of a layer mostly walks along with the loss of the optical quality, a statement about the permanence of the system can be also done in this manner. The brilliant measurements were carried out under Einstrahlwinkeln by 20 DEG , 60 DEG and 85 DEG.

The results are in Fig. 11 and Fig. 12 shown. They confirm the visual judgement of the tests. System IV suffers during the Bewitterungsphase practically no brilliant loss. The shine rises even at first something, before he goes back after 1000 h again easily.

#### Micromechanical investigations

To receive a very comprehensive picture of the changes by the load in the QUV B test, were characterised unbewitterte and bewitterte tests also with the help of the mike hardness measurement.

The Fig. 13 and 14 show that neither the universal hardness nor the sculptural universal hardness change by the Bewitterung drastically.

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#### Claims of DE19910876

1. Procedure is produced to the production of a bewitterungsbeständigen coating on substrates like glass surfaces, metal surfaces or polymer surfaces with on the substrate a coating by hydrolytische condensation at least of one hydrolysierbaren silicon connection, thereby marked that the hydrolytische condensation with 20-100 Mol-%, covered to the monomeren source components, with a hydrolysierbaren silicon connection of the general formula I

$X_m-Si-R_4-m-Y_n$  I

it is carried out and X can have passed away immediately or and hydrogen, halogen, Alkoxy, Acyloxy, Alkylcarbonyl, Alkoxycarbonyl or NO. ' 2 (R '-H and/or Alkyl) signify and the rests R which immediately or can have passed away, Alkyl, Alkenyl, Alkynyl, Aryl, Arylalkyl, Alkylaryl, Arylalkenyl, Alkenylaryl, Arylalkynyl or Alkynylaryl explain and these rests can be interrupted by O- or S. atoms or the GROUP NO. ' or-N (H) C (O) O (old ethane) and one or several Substituenten from the group of the halogens and if necessary substituted Amino-, Amid-, aldehyde, Keto-, Alkylcarbonyl-, Carboxy-, Mercapto-, Cyano-, Hydroxy-, Alkoxy-, Alkoxycarbonyl-Sulfonsäure-, phosphorus acid, Acryloxy-, Methacryloxy-, Epoxy or vinyl groups can carry and Y blocked Isocyanat is, with m = from 1 to 3 and n = from 1 to 3.

2. Procedures after claim 1, thereby marked that to the blocking of the Isocyanats Dimethylpyrazol, Butanonoxim, Acetonoxim, Malonsäuredialkylester, ELEMENT-Caprolactam is used.

3. Procedures after claim 1 or 2, thereby marked, that the Hydrolyse in present from 0-80 Mol-% of an other silicon connection of the general formula II

$X_m-Si-R_4-m-Zn$  II

it is carried out and X, R, m in the patent claim own 1 given meaning and n = 1-4 is as well as Z = OH, NH<sub>2</sub>, NH (CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> or an Epoxyfunktion is.

4. Procedures after at least one of the claims from 1 to 3, thereby marked, that the Hydrolyse in present from 0-40 Mol-% of a metal connection of the general formula III

MeRx

it is carried out and Me for titan, zircon, tin or aluminium, is on a par and can have passed away R this or, is selected from halogen, Alkoxy, Alkoxy carbonyl and Hydroxy and some of these rests can be substituted all or part with a Chelatliganden and X for Al<sup>3</sup> and for Ti and Zr<sup>4</sup> is.

5. Procedures after at least one of the claims from 1 to 4, thereby marked, that the Hydrolyse in present of an other connection of the general formula IV

R-X<sub>p</sub> IV

it is carried out and R stands for an organic not silicon-containing rest and X = OH, NH<sub>2</sub> or an Anhydrid is, with p = from 1 to 5, mainly p = from 1 to 3, especially prefers p = 2.

6. Procedures after at least one of the claims from 1 to 5, thereby marked that the hydrolysierbare silicon connection of the general formula I perch preferentially with DMP or 1,2,4-Triazol. 3-Isocyanatopropyltriethoxysilan is.

7. Procedures after at least one of the claims from 1 to 6, thereby marked that the hydrolysierbare silicon connection of the general formula II is preferentially 3Aminopropyl-triethoxysilan, 3Glycidyloxypropyl-trimethoxysilan, DAMO.

8. Procedures after at least one of the claims from 1 to 7, thereby marked that the connection of the general formula IV is preferentially BTCA, THEIC, HBPA.

9. Procedures after at least one of the claims from 1 to 8, thereby marked that the hydrolytische condensation is carried out in present of a sour, basischen or metal-organic condensation catalyst.

10. Procedures are selected after at least one of the claims from 1 to 9, thereby marked that are added with the Hydrolyse additives them from organic connections, course means, colouring, UV stabilizers, fillers, viscosity regulators, lubricants, net means, Antiabsetzmitteln and/or oxidation inhibitors or mixtures of it.

11. Procedure is precleaned after at least one of the claims from 1 to 10, thereby marked that the substrate surface treats before the Aufbringung of the coating material with a Primer ausgeheizt, erodedly, by means of watery or organic media and/or is put out to an electric unloading.

12. Procedures after at least one of the claims from 1 to 11, thereby marked that the coating is hardened by warm treatment at a temperature to 300 C DEG mainly from 110 to 240 C DEG and/or by treatment with radiation mainly IR, electron beams, UV or microwaves.